IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of	:	**Confirmation No. 5123**
Hisashi ISAKA et al.	:	Docket No. 2002-0382A
Serial No. 10/088,265	:	Group Art Unit 1615
Filed March 18, 2002	:	Examiner P. Short

POLYORTHOESTER AND CURABLE COMPOSITION CONTAINING THE SAME

DECLARATION

Commissioner for Patents
P. O. Box 1450
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Sir:

I, Akiko KOJIMA, declare and say:

that I am thoroughly conversant in both the Japanese and English languages;

that I am presently engaged as a translator in these languages;

that the attached document represents a true English translation of the Japanese Priority Application No. 300894/99, filed October 22, 1999.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 10th day of May, 2004.

Akiko Kojima

Akiko KOJIMA

(TRANSLATION)

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application : October 22, 1999

Application Number: Patent Application No. 300894/99

Applicant(s) : Kansai Paint Co., Ltd.

October 13, 2000

Kozo OIKAWA

Commissioner,
Patent Office

Certification Number 2000-3083256

[Document Name] Patent Application

[Reference Number] 9910084

[Filing Date] October 22, 1999

[Submitted to] Commissioner, Patent Office

[International Classification] C09D

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[Indication of Official Fees]

[Number of Prepayment] 019666

[Amount of Payment] 21000

[List of Submitted Objects]

[Name of Object] Specification 1

[Name of Object] Abstract 1

[Proofing] Required

[Document Name] Specification

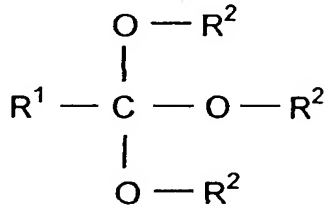
[Title of the Invention] Curable Composition

[Claims]

[Claim 1] A curable composition comprising:

[A] a polyorthoester prepared by reacting:

(a) an orthoester represented by the following Formula (1):



(1)

wherein R^1 represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and three R^2's may be the same or different and each represent an alkyl group having 1 to 4 carbon atoms,

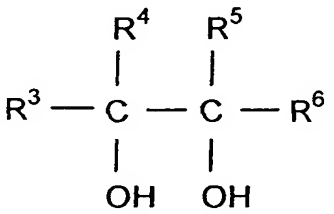
(b) at least one glycol compound selected from α-glycols and β-glycols, and

(c) a hydroxyl group-containing compound having at least two hydroxyl groups in a molecule other than the above (b); and

[B] a compound having at least two groups having a reactivity with a hydroxyl group in a molecule.

[Claim 2] The curable composition as set forth in Claim 1, wherein the orthoester (a) is at least one compound selected from methyl orthoformate, ethyl orthoformate, methyl orthoacetate and ethyl orthoacetate.

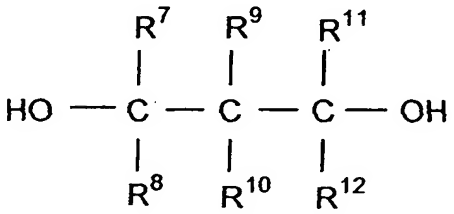
[Claim 3] The curable composition as set forth in Claim 1 or 2, wherein the glycol compound (b) is at least one glycol compound selected from an α-glycol represented by the following Formula (2):



(2)

wherein R^3, R^4, R^5 and R^6 may be the same or different and each represent a hydrogen atom, an alkyl group having 1 to 24 carbon atoms, an aralkyl group having 7 to 24 carbon atoms or a phenyl group, or a group obtained by substituting a part of these groups with an oxygen atom, and the total of the carbon atoms in the groups represented by R^3, R^4, R^5 and R^6 falls in a range of 0 to 24; and R^4 and R^5 may form a cyclic structure together with carbon atoms to which they are bonded directly, and

a β-glycol represented by the following Formula (3):



(3)

wherein R^7, R^8, R^9, R^{10}, R^{11} and R^{12} may be the same or different and each represent a hydrogen atom, an alkyl group having 1 to 24 carbon atoms, an aralkyl group having 7 to 24 carbon atoms or a phenyl group, or a group obtained by substituting a part of these groups with an oxygen atom, and the total of the carbon atoms in the groups represented by R^7, R^8, R^9, R^{10}, R^{11} and R^{12} falls in a range of 0 to 24; and R^7 and R^9 or R^7, R^9 and R^{11} may form a cyclic structure together with carbon atoms to which they are bonded directly.

[Claim 4] The curable composition as set forth in any one of Claims 1 to 3, wherein the glycol compound (b) is at least one compound selected from ethylene glycol, 1,2-propylene glycol, 1,2-hexanediol, neopentyl glycol, 2-methyl-1,3-propanediol, 2-methyl-2,4-pentanediol, 3-methyl-1,3-butanediol, 2-ethyl-1,3-hexanediol, 2,2-diethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol and 2-butyl-2-ethyl-1,3-propanediol.

[Claim 5] The curable composition as set forth in any one of Claims 1 to 4, wherein the hydroxyl group-containing compound (c) has a molecular weight falling in a range of 90 to 100,000 and a hydroxyl group value falling in a range of 20 to 1,850.

[Claim 6] The curable composition as set forth in any one of Claims 1 to 5,

wherein a hydroxyl group contained in the hydroxyl group-containing compound (c) is blocked by an orthoester of a 5-membered ring or a 6-membered ring constituted by the orthoester (a) and the glycol compound (b).

[Claim 7] The curable composition as set forth in any one of Claims 1 to 6, wherein the compound [B] is at least one compound or resin selected from polyisocyanate compounds, amino resins, epoxy group-containing compounds, alkoxysilyl group-containing compounds and compounds having two or more carboxylic anhydride groups.

[Claim 8] The curable composition as set forth in any one of Claims 1 to 7, further comprising an acid catalyst.

[Detailed Description of the Invention]

[0001]

[Technical field to which the invention belongs]

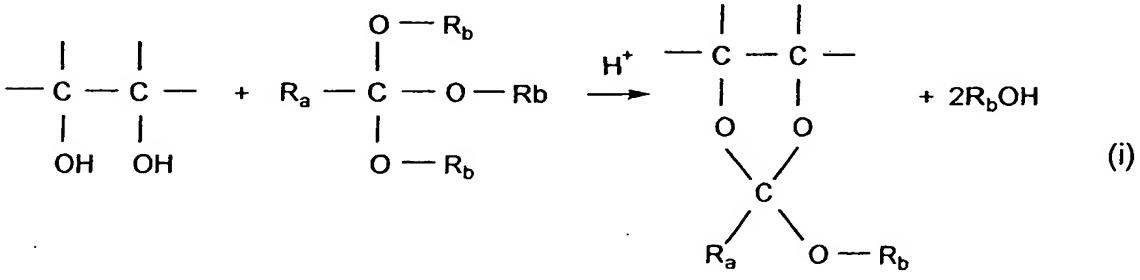
The present invention relates to a novel curable composition containing a polyorthoester and a curing agent, more specifically to a curable composition which can be reduced in viscosity and increased in solid content.

[0002]

[Prior art and its problem]

An orthoester has so far been used as a dehydrating agent and a synthetic raw material for various compounds. Further, an orthoester is known as a protective group for a hydroxyl group and protects a hydroxyl group on such moderate conditions as a room temperature in the presence of an acid catalyst by reaction as shown in the following Equation (i):

[0003]



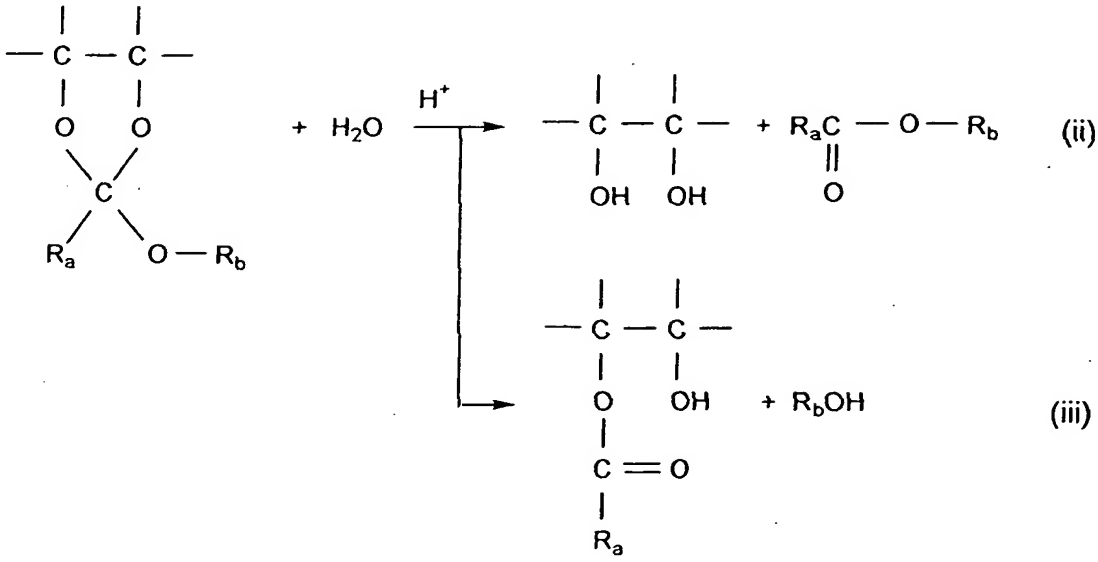
(i)

[0004]

The protected hydroxyl group is stable under a base condition, but the protective group is readily desorbed under an acid condition by hydrolysis

as shown in the following Equation (ii) or (iii):

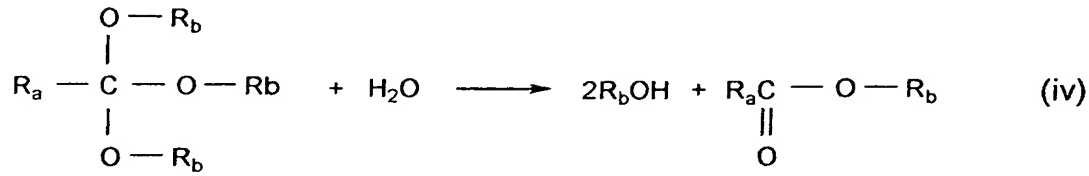
[0005]



[0006]

In general, an orthoester is easily hydrolyzed to form two molecules of alcohol and one molecule of ester:

[0007]



[0008]

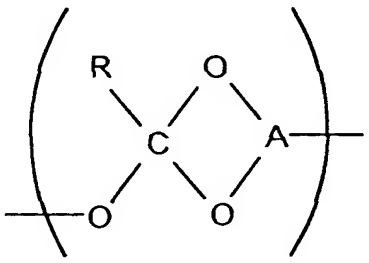
Proposed are several techniques on a polyorthoester industrially making use of such characteristics of the polyorthoester described above. For example, a polyorthoester for a photoresist is described in Japanese Patent Publication No.20325/1988, and a polyorthoester for drug delivery is described in Japanese Patent Application Laid-Open No.502465/1993.

[0009]

The polyorthoesters described in these official gazettes are compounds which are obtained by condensing triols with orthoesters and which have a specific repetitive unit, for example, a repetitive unit represented by the following Formula (v). However, in producing this compound, only specific triol

can be used as a hydroxy group-containing compound, and it has a degree of a freedom only in such an extent that a molecular weight can be changed by a blending ratio of the triol to the orthoester, so that there is the problem that a degree of freedom in molecular design is low.

[0010]



(v)

[0011]

Further, a polymer having a spiroorthoester structure is described in Japanese Patent Application Laid-Open No.42724/1982, and it is shown that the above polymer is a cross-linking high polymer having a small volumetric shrinkage. However, caprolactone is essentially used as a raw material, and therefore, a degree of freedom in molecular design is low. Furthermore, a polymer having a bicycloorthoester structure is described in Japanese Patent Application Laid-Open No.233114/1985, and it is shown that the above polymer is a cross-linking high polymer having an excellent balance between an elastic modulus and a toughness. However, trimethylolpropane or trimethylolethane is essentially used as a raw material, and therefore, involved therein is the problem that a degree of freedom in molecular design is low.

[0012]

It is known, as described above, that an alkoxy group of an orthoester is subjected to alcohol exchange reaction with a hydroxyl group in the presence of an acid catalyst, and a 5-membered ring, a 6-membered ring or a bicyclo ring can be formed by using a hydroxyl group-containing compound in which two hydroxyl groups are close. Making use of this property, an orthoester is used as a protective group for close hydroxyl groups mainly in the biochemical field.

[0013]

Three alkoxy groups of an orthoester can be subjected to alcohol

exchange reaction, and it can be turned into a polyorthoester by combining with polyhydric alcohol. In this case, if an orthoester is subjected merely to exchange reaction with polyhydric alcohol (condensation reaction by dealcohol), it is gelatinized by converting into three dimension.

[0014]

Further, a curable resin composition prepared by combining a polyhydric hydroxyl group-containing compound or a resin with a curing agent has so far been known, and the above curable resin composition has the problems that it is increased in viscosity which originates in a hydroxyl group and reduced in compatibility; it is increased in polarity and deteriorated in wetting property when coated on a base material; and it is inferior in storage stability when mixed with a curing agent having a reactivity with a hydroxyl group such as a polyisocyanate compound at a room temperature.

[0015]

An object of the present invention is to provide a curable composition using a polyorthoester having a high degree of freedom in molecular design and a low viscosity and capable of being readily controlled in a molecular weight, in which there involved is no problem originating in a hydroxyl group, for example, a problem on an increase in viscosity of the curable composition; the solid content can be elevated; and the compatibility, the wetting property to a base material and the storage stability are good.

[0016]

[Means to solve the problems]

The present inventors repeated intensive investigations in order to solve the above problems. As a result, they found that the above problems could be solved by combining a curing agent with a polyorthoester prepared by reacting a specific glycol compound, an orthoester and a polyhydric hydroxyl group-containing compound, and they have come to complete the present invention.

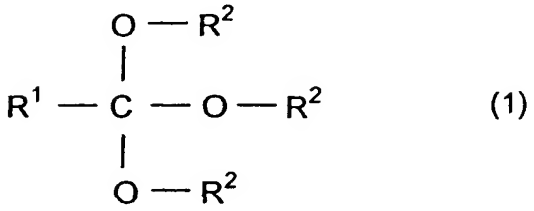
[0017]

That is, the present invention provides a curable composition comprising:

[A] a polyorthoester prepared by reacting:

(a) an orthoester represented by the following Formula (1):

[0018]



(1)

[0019]

wherein R^1 represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and three R^2's may be the same or different and each represent an alkyl group having 1 to 4 carbon atoms,

(b) at least one glycol compound selected from α-glycols and β-glycols, and

(c) a hydroxyl group-containing compound having at least two hydroxyl groups in a molecule other than the above (b); and

[B] a compound having at least two groups having a reactivity with a hydroxyl group in a molecule.

[0020]

The curable composition of the present invention shall be explained below in further details.

[0021]

[Mode for carrying out the invention]

Polyorthoester [A]

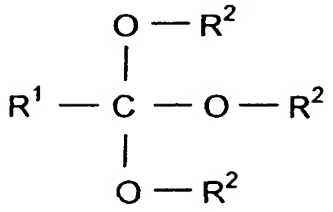
The polyorthoester [A] which is the component [A] in the present invention is a reaction product of the orthoester (a), the glycol compound (b) and the hydroxyl group-containing compound (c) each described below.

[0022]

Orthoester (a):

The orthoester which is the component (a) is a compound represented by the following Formula (1):

[0023]



(1)

[0024]

wherein R^1 represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and three R^2's may be the same or different and each represent an alkyl group having 1 to 4 carbon atoms.

[0025]

In Formula (1) described above, the alkyl group having 1 to 4 carbon atoms represented by R^1 or R^2 is linear or branched and includes, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and t-butyl.

[0026]

The specific examples of the orthoester (a) include, for example, methyl orthoformate, ethyl orthoformate, propyl orthoformate, butyl orthoformate, methyl orthoacetate, ethyl orthoacetate, methyl orthopropionate, ethyl orthopropionate, methyl orthobutyrate and ethyl orthobutyrate. Among them, methyl orthoformate, ethyl orthoformate, methyl orthoacetate and ethyl orthoacetate are suited. They may be used alone or in combination of two or more kinds thereof.

[0027]

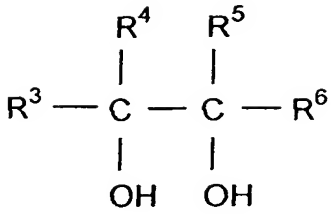
Glycol compound (b):

The glycol compound which is the component (b) is at least one glycol compound selected from α-glycols and β-glycols having two hydroxyl groups in a molecule.

[0028]

Among them, a compound represented by the following Formula (2) can suitably be used as the α-glycol:

[0029]



(2)

[0030]

wherein R^3, R^4, R^5 and R^6 may be the same or different and each represent a hydrogen atom, an alkyl group having 1 to 24 carbon atoms, an aralkyl group having 7 to 24 carbon atoms or a phenyl group, or a group obtained by substituting a part of these groups with an oxygen atom, and the total of the carbon atoms in the groups represented by R^3, R^4, R^5 and R^6 falls in a range of 0 to 24, preferably 0 to 10; and R^4 and R^5 may form a cyclic structure together with carbon atoms to which they are bonded directly.

[0031]

In Formula (2) described above, the alkyl group having 1 to 24 carbon atoms represented by R^3, R^4, R^5 or R^6 is linear, branched or cyclic and includes methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, pentyl, hexyl, n-octyl, 2-ethylhexyl, decyl, dodecyl, octadecyl, cyclohexyl, methylcyclohexyl, cyclohexylmethyl and cyclohexylethyl.

[0032]

In Formula (2) described above, the aralkyl group having 7 to 24 carbon atoms represented by R^3, R^4, R^5 or R^6 is preferably an alkyl group substituted with phenyl, and the specific examples thereof include benzyl and phenethyl.

[0033]

In Formula (2) described above, the group obtained by substituting a part of the alkyl group, the aralkyl group or the phenyl group, represented by R^3, R^4, R^5 or R^6, with an oxygen atom includes, for example, an alkoxyalkyl group such as methoxymethyl, ethoxymethyl, propoxymethyl and butoxymethyl; an alkanoyloxyalkyl group such as acetoxymethyl and acetoxyethyl; and an aryloxyalkyl group such as phenoxymethyl and phenoxyethyl.

[0034]

Among them, R^3, R^4, R^5 or R^6 in Formula (2) described above is

preferably a hydrogen atom or an alkyl group having 1 to 6 carbon atoms.

[0035]

In Formula (2) described above, the cyclic structure which can be formed by R^4 and R^5 together with carbon atoms to which they are bonded directly includes, for example, a cyclohexyl group and a cyclopentyl group.

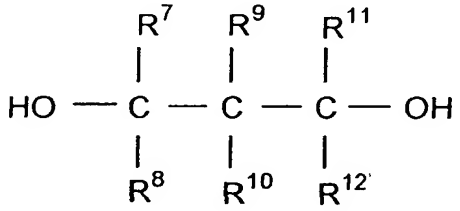
[0036]

Thus, the representative examples of the α-glycols include, for example, ethylene glycol, 1,2-propylene glycol, 1,2-butylene glycol, 2,3-butylene glycol, 1,2-hexanediol, 1,2-dihydroxycyclohexane, pinacol and hydrolysis products of long chain alkyl monoepoxides; fatty acid monoglycerides (α products) such as glycerin monoacetate (α product) and glycerin monostearate (α product); and 3-ethoxypropane-1,2-diol and 3-phenoxypropane-1,2-diol. Among them, ethylene glycol, 1,2-propylene glycol and 1,2-hexanediol are suited.

[0037]

On the other hand, particularly a compound represented by the following Formula (3) can suitably be used as the β-glycol:

[0038]



(3)

[0039]

wherein R^7, R^8, R^9, R^{10}, R^{11} and R^{12} may be the same or different and each represent a hydrogen atom, an alkyl group having 1 to 24 carbon atoms, an aralkyl group having 7 to 24 carbon atoms or a phenyl group, or a group obtained by substituting a part of these groups with an oxygen atom, and the total of the carbon atoms in the groups represented by R^7, R^8, R^9, R^{10}, R^{11} and R^{12} falls in a range of 0 to 24; and R^7 and R^9 or R^7, R^9 and R^{11} may form a cyclic structure together with carbon atoms to which they are bonded directly.

[0040]

In Formula (3) described above, the alkyl group having 1 to 24

carbon atoms represented by R^7, R^8, R^9, R^{10}, R^{11} or R^{12} includes the same ones as those described above as the alkyl group represented by R^3, R^4, R^5 or R^6 in Formula (2) described above.

[0041]

In Formula (3) described above, the aralkyl group having 7 to 24 carbon atoms represented by R^7, R^8, R^9, R^{10}, R^{11} or R^{12} is preferably an alkyl group substituted with phenyl, and the specific examples thereof include benzyl and phenethyl.

[0042]

In Formula (3) described above, the group obtained by substituting a part of the alkyl group, the aralkyl group or the phenyl group, represented by R^7, R^8, R^9, R^{10}, R^{11} or R^{12}, with an oxygen atom includes, for example, an alkoxyalkyl group such as methoxymethyl, ethoxymethyl, propoxymethyl and butoxymethyl; an alkanoyloxyalkyl group such as acetoxymethyl and acetoxyethyl; and an aryloxyalkyl group such as phenoxymethyl and phenoxyethyl.

[0043]

In Formula (3) described above, the cyclic structure which can be formed by R^7 and R^9 or R^7, R^9 and R^{11} together with carbon atoms to which they are bonded directly includes, for example, a cyclohexyl group and a cyclopentyl group.

[0044]

Among them, R^7, R^8, R^9, R^{10}, R^{11} or R^{12} in Formula (3) described above is preferably a hydrogen atom or an alkyl group having 1 to 6 carbon atoms.

[0045]

Thus, the representative examples of the β-glycols include, for example, neopentyl glycol, 2-methyl-1,3-propanediol, 2-methyl-2,4-pentanediol, 3-methyl-1,3-butanediol, 2-ethyl-1,3-hexanediol, 2,2-diethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol, 2-butyl-2-ethyl-1,3-propanediol, 2-phenoxypropane-1,3-diol, 2-methyl-2-phenylpropane-1,3-diol, 1,3-propylene glycol, 1,3-butylene glycol, dimethylolpropionic acid, dimethylolbutanoic acid, 2-ethyl-1,3-octanediol and 1,3-dihydroxycyclohexane; and fatty acid

monoglycerides (β products) such as glycerin monoacetate (β product) and glycerin monostearate (β product). Among them, suited are neopentyl glycol, 2-methyl-1,3-propanediol, 2-methyl-2,4-pentanediol, 3-methyl-1,3-butanediol, 2-ethyl-1,3-hexanediol, 2,2-diethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol and 2-butyl-2-ethyl-1,3-propanediol.

[0046]

(c) Hydroxyl group-containing compound:

The hydroxyl group-containing compound which is the component (c) is a compound having at least two hydroxyl groups in a molecule other than the glycol compound (b) described above.

[0047]

The hydroxyl group-containing compound (c) includes compounds having two hydroxyl groups other than α-glycols and β-glycols, or compounds having 3 or more hydroxyl groups in a molecule.

[0048]

The compounds having two hydroxyl groups other than α-glycols and β-glycols include, for example, 1,4-butanediol, 1,4-dihydroxycyclohexane, 1,5-pentanediol, 1,6-hexanediol, 2,5-hexanediol, 3-methyl-1,5-pentanediol, 1,4-dimethylolcyclohexane, tricyclodecanedimethanol, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate (this compound corresponds to ester of hydroxypivalic acid and neopentyl glycol), bisphenol A, bisphenol F, bis(4-hydroxyhexyl)-2,2-propane, bis(4-hydroxyhexyl)methane, 3,9-bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro[5,5]undecane, diethylene glycol, triethylene glycol, tetra- or more polyethylene glycol, dipropylene glycol, tripropylene glycol, tetra- or more polypropylene glycol, copolymers having hydroxyl groups at both terminals obtained by copolymerizing ethylene oxide with propylene oxide, linear polyesters having hydroxyl groups at both terminals such as polycaprolactonediol, polycarbonatediol and carboxylic acid adducts of diepoxide.

[0049]

The compounds described above having 3 or more hydroxyl groups include, for example, glycerin, diglycerin, triglycerin, pentaerythritol, dipentaerythritol, sorbitol, mannit, trimethylolethane, trimethylolpropane,

ditrimethylolpropane, tris(2-hydroxyethyl)isocyanurate, gluconic acid and polymers having 3 or more hydroxyl groups (polyesters, polyethers, acryl polymers, ketone resins, phenol resins, epoxy resins, urethane resins those having 3 or more hydroxyl groups; polyvinyl alcohols which are saponified products of polyvinyl acetates; and natural saccharides such as glucose).

[0050]

Capable of being suitably used as the hydroxyl group-containing compound (c) are the compounds having a hydroxyl group value falling in a range of 20 to 1,850 mg KOH/g, particularly 40 to 1,650 mg KOH/g.

Production of polyorthoester [A]:

In producing the polyorthoester [A] which is one component of the composition of the present invention, a blending ratio of the orthoester (a), the glycol compound (b) and the hydroxyl group-containing compound (c) shall not specifically be restricted. In general, it is suitable, in terms of an easiness in controlling the molecular weight, to use the orthoester (a) in a proportion falling in a range of 0.01 to 10 moles, preferably 0.05 to 5 moles and more preferably 0.1 to 2 moles; and the glycol compound (b) in a proportion falling in a range of 0.01 to 10 moles, preferably 0.05 to 5 moles and more preferably 0.1 to 2 moles, each per equivalent of a hydroxyl group contained in the hydroxyl group-containing compound (c).

[0051]

The polyorthoester [A] can be obtained by subjecting the three components (a), (b) and (c) described above to condensation reaction. For example, it can suitably be produced by heating the three components described above at a temperature falling in a range of usually a room temperature to 250°C, preferably 70 to 200°C for approximately 1 to 20 hours, if necessary, in the presence of an organic solvent and an acid catalyst to subject them to condensation reaction.

[0052]

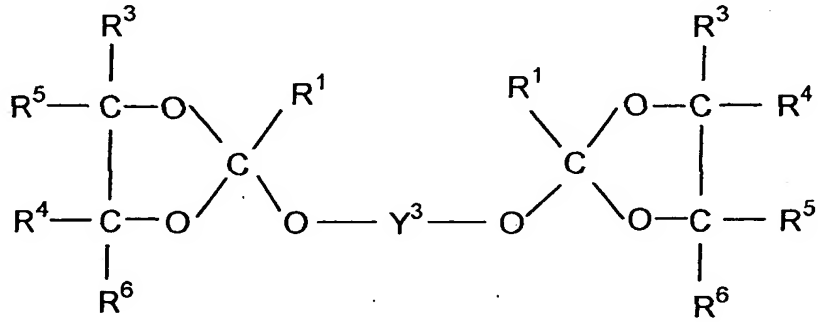
In the reaction described above, an alkoxy group of the orthoester (a) causes exchange reaction with the alcohol parts of the glycol compound (b) and the hydroxyl group-containing compound (c). In this case, the orthoester (a) is preferentially reacted with the α-glycol or β-glycol which is the glycol

compound (b) having hydroxyl groups close to each other to form a cyclic structure. That is, the glycol compound (b) is cyclized by preferentially reacting with two functional groups (alkoxyl groups) of the orthoester (a) which is trifunctional. The remaining one alkoxyl group of the orthoester is reacted with the hydroxyl group-containing compound (c). Thus, cross-linking between the molecules is not brought about in producing the polyorthoester [A], and therefore, the product can be inhibited from being increased in molecular weight and viscosity. On the other hand, if the orthoester (a) is reacted directly with the hydroxyl group-containing compound (c) in the absence of the glycol compound (b), cross-linking between the molecules takes place, so that the product is rapidly increased in molecular weight and viscosity. The polyorthoester [A] in the composition of the present invention is a product which is inhibited from being increased in molecular weight and viscosity by further adding the glycol compound (b) to the orthoester (a) and the hydroxyl group-containing compound (c) to react them.

[0053]

When used as the raw materials are, for example, the orthoester represented by Formula (1) described above, the α-glycol represented by Formula (2) described above and the compound having 2 hydroxyl groups in a molecule, the polyorthoester [A] produced in the manner described above can have a structure represented by the following Formula (4):

[0054]



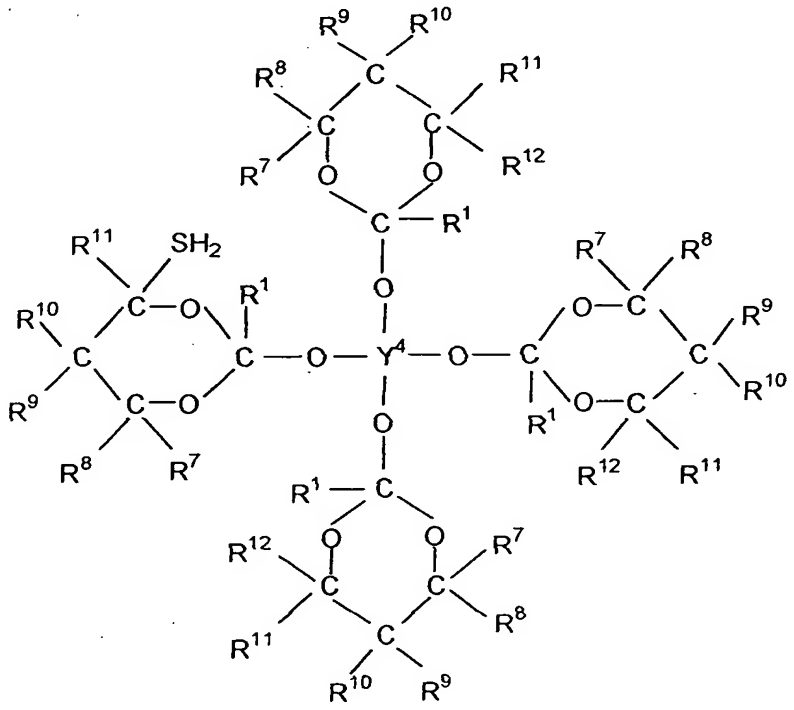
(4)

[0055]

wherein Y^1 represents a residue obtained by removing, from the compound having 2 hydroxyl groups in a molecule, the 2 hydroxyl groups; and R^1, R^3, R^4, R^5 and R^6 are the same as defined above. Also, when used as the raw

materials are, for example, the orthoester represented by Formula (1) described above, the β–glycol represented by Formula (3) described above and the compound having 4 hydroxyl groups in a molecule, the polyorthoester [A] produced in the manner described above can have a structure represented by the following Formula (5):

[0056]



(5)

[0057]

wherein Y^2 represents a residue obtained by removing, from the compound having four hydroxyl groups in a molecule, the four hydroxyl groups; and R^1, R^7, R^8, R^9, R^{10}, R^{11} and R^{12} are the same as defined above.

[0058]

Compound [B] having at least two groups having a reactivity with a hydroxyl group in a molecule

A compound having at least two groups having a reactivity with a hydroxyl group in a molecule (hereinafter, referred to as a "compound [B]") which is the component [B] in the composition of the present invention, is a compound having a reactivity with a hydroxyl group and can be reacted with a hydroxyl group formed by hydrolysis of an orthoester group in the polyorthoester [A] to form a cured matter.

[0059]

Capable of being given as the representative examples of the compound [B] are, for example, polyisocyanate compounds, amino resins, epoxy group-containing compounds, alkoxysilyl group-containing compounds and compounds having two or more carboxylic anhydride groups.

[0060]

The polyisocyanate compounds described above include all of compounds in which isocyanato groups (NCO group) are not blocked (hereinafter abbreviated as "non-blocked polyisocyanate compound") and compounds in which isocyanato groups are partially or completely blocked (hereinafter abbreviated as "blocked polyisocyanate compound").

[0061]

The non-blocked polyisocyanate compounds include, for example, aliphatic diisocyanates such as lysine diisocyanate, hexamethylene diisocyanate and trimethylhexane diisocyanate; alicyclic diisocyanates such as hydrogenated xylilene diisocyanate, isophorone diisocyanate, methylcyclohexane-2,4 or 2,6-diisocyanate, 4,4'-methylenebis(cyclohexylisocyanate) and 1,3-(isocyanatomethyl)cyclohexane; aromatic diisocyanates such as tolylene diisocyanate, xylylene diisocyanate and diphenylmethane diisocyanate; organic polyisocyanates including trivalent or more polyisocyanates such as lysine triisocyanate, adducts of these organic polyisocyanates to polyhydric alcohols, low molecular weight polyester resins or water, cyclic polymers (for example, isocyanurate) of the respective organic diisocyanates themselves described above, and biuret type adducts thereof.

[0062]

The blocked polyisocyanate compounds are obtained by blocking the isocyanato groups of the non-blocked polyisocyanate compounds described above with a blocking agent. Capable of being suitably used as the blocking agent described above are, for example, blocking agents including phenol bases such as phenol, cresol and xylenol; lactam bases such as ε-caprolactam, δ-valerolactam, γ-butyrolactam and β-propiolactam; alcohol bases such as methanol, ethanol, n- or i-propyl alcohol, n-, i- or t-butyl alcohol, ethylene glycol

monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, propylene glycol monomethyl ether and benzyl alcohol; oxime bases such as formamidoxime, acetaldoxime, acetoxime, methyl ethyl ketoxime, diacetylmonoxime, benzophenoneoxime and cyclohexaneoxime; and active methylene bases such as dimethyl malonate, diethyl malonate, ethyl acetoacetate, methyl acetoacetate and acetylacetone. The isocyanato groups of the polyisocyanates can readily be blocked by mixing the non-blocked polyisocyanate compounds described above with the blocking agents described above.

[0063]

These polyisocyanate compounds can be used alone or in combination of two or more kinds thereof.

[0064]

The amino resins which can be used as the compound [B] include, for example, methylol amino resins obtained by reacting aldehydes with amino components such as melamine, urea, benzoguanamine, acetoguanamine, steroguanamine, spiroguanamine and dicyanediamide. The aldehydes described above include, for example, formaldehyde, paraformaldehyde, acetaldehyde and benzaldehyde. Further, compounds obtained by etherifying these methylol melamine resins with at least one alcohol are included in the amino resins described above. The alcohols used for the etherification include, for example, monohydric alcohols such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, 2-ethylbutanol and 2-ethylhexanol. Among them, particularly suited are the melamine resins obtained by etherifying at least a part of the methylol groups of the methylol melamine resins with the monohydric alcohols having 1 to 4 carbon atoms.

[0065]

Capable of being given as the specific examples of the melamine resins described above are, for example, methyl-etherified melamine resins such as Cymel 300, ditto 303, ditto 325, ditto 327, ditto 350, ditto 730, ditto 736 and ditto 738 (all described above are manufactured by Mitsui Cytec Co., Ltd.),

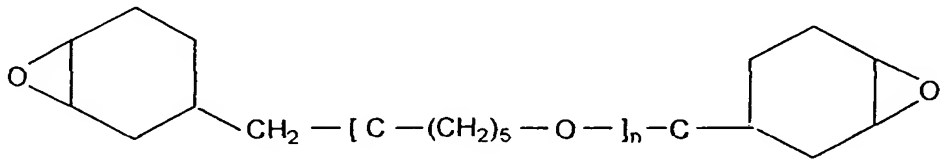
Melan 522 and ditto 523 (all described above are manufactured by Hitachi Chemical Co., Ltd.), Nikalac MS001, ditto MX430 and ditto MX650 (all described above are manufactured by Sanwa Chemical Co., Ltd.), Sumimal M-55, ditto M-100 and ditto M-40S (all described above are manufactured by Sumitomo Chemical Ind. Co., Ltd.) and Resimine 740 and ditto 747 (all described above are manufactured by Monsanto Co., Ltd.); butyl-etherified melamine resins such as U-van 20SE and ditto 225 (all described above are manufactured by Mitsui Toatsu Co., Ltd.) and Super Beckamine J820-60, ditto L-117-60, ditto L-109-65, ditto 47-508-60, ditto L-118-60 and ditto G821-60 (all described above are manufactured by Dainippon Ink & Chemicals Ind. Co., Ltd.); and methyl ether and butyl ether-mixed etherified melamine resins such as Cymel 232, ditto 266, ditto XV-514 and ditto 1130 (all described above are manufactured by Mitsui Cytec Co., Ltd.), Nikalac MX500, ditto MX600 ditto MS35 and ditto MS95 (all described above are manufactured by Sanwa Chemical Co., Ltd.), Resimine 753 and ditto 755 (all described above are manufactured by Monsanto Co., Ltd.) and Sumimal M-66B (manufactured by Sumitomo Chemical Ind. Co., Ltd.). These melamine resins can be used alone or in combination of two or more kinds thereof.

[0066]

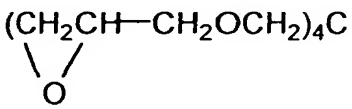
The epoxy group-containing compound which can be used as the compound [B] is a compound having two or more epoxy groups in a molecule, and the representative examples thereof include ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, tripropylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, 1,4-butanediol diglycidyl ether, neopentyl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerin diglycidyl ether, diglycerin tetraglycidyl ether, trimethylolpropane triglycidyl ether, 2,6-diglycidyl phenyl ether, sorbitol triglycidyl ether, triglycidyl isocyanurate, diglycidylamine, diglycidylbenzylamine, diglycidyl phthalate, bisphenol A diglycidyl ether, butadiene dioxide, dicyclopentadiene dioxide, diester of 3,4-epoxycyclohexenecarboxylic acid and ethylene glycol, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexanecarboxylate, bis(3,4-epoxycyclohexylmethyl) adipate, glycidyl ether of dicyclopentadieneol

epoxide, dipentene dioxide, adducts of bisphenol A type epoxy resins and ethylene oxide, Epoleade GT300 (trifunctional alicyclic epoxy compound, manufactured by Daicel Chemical Industries Ltd.), Epoleade GT400 (tetrafunctional alicyclic epoxy compound, manufactured by Daicel Chemical Industries Ltd.); Epoleade GT301, ditto GT302 and ditto GT303 (ring-opened ε-caprolactone chain-containing trifunctional alicyclic epoxy compounds, all described above are manufactured by Daicel Chemical Industries Ltd.); Epoleade GT401, ditto GT402 and ditto GT403 (ring-opened ε-caprolactone chain-containing tetrafunctional alicyclic epoxy compounds, all described above are manufactured by Daicel Chemical Industries Ltd.); Epikote 828, ditto 834 and ditto 100 (bisphenol A type epoxy resins, all described above are manufactured by Yuka Shell Epoxy Co., Ltd.); Epikote 154 (cresol novolak type epoxy resin, manufactured by Yuka Shell Epoxy Co., Ltd.); Celloxide 2081, ditto 2082 and ditto 2083 each represented by the following Formula (6) (all described above are manufactured by Daicel Chemical Industries Ltd.; in the following Formula (6), the product in which n is 1 is Celloxide 2081, the product in which n is 2 is Celloxide 2082, and the product in which n is 3 is Celloxide 2083); and Denacol EX-411 represented by the following Formula (7) (manufactured by Nagase Kasei Co., Ltd.):

[0067]



(6)



(7)

[0068]

In Formula (6), n represents an integer of 1 to 3.

[0069]

The epoxy group-containing compound described above includes

copolymers of epoxy group-containing polymerizable unsaturated monomers such as glycidyl (meth)acrylate, allyl glycidyl ether and 3,4-epoxycyclohexylmethyl (meth)acrylate with other polymerizable unsaturated monomers. The other polymerizable unsaturated monomers described above include, for example, C_1 to C_{24} alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl acrylate, n-octyl (meth)acrylate, lauryl (meth)acrylate, tridecyl (meth)acrylate and stearyl (meth)acrylate; monoesters of polyhydric alcohols and acrylic acid or methacrylic acid such as 2-hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, 2,3-dihydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate and polyethylene glycol mono(meth)acrylate; compounds obtained by subjecting ε-caprolactone to ring opening reaction with the monoesters of the polyhydric alcohols described above and acrylic acid or methacrylic acid; alkoxysilyl group-containing polymerizable unsaturated compounds such as vinyltrimethoxysilane, vinyltriethoxysilane, vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, γ-(meth)acryloyloxypropyltrimethoxysilane, γ-(meth)acryloyloxypropylmethyldimethoxysilane, γ-(meth)acryloyloxypropylmethyldiethoxysilane, γ-(meth)acryloyloxypropyltriethoxysilane, β-(meth)acryloyloxyethyltrimethoxysilane and γ-(meth)acryloyloxybutylphenyldimethoxysilane; acrylonitrile, methacrylonitrile, tricyclodecanyl (meth)acrylate, isobornyl (meth)acrylate, vinyl acetate, Beova Monomer (manufactured by Shell Chemical Co., Ltd.), styrene, vinyltoluene and α-methylstyrene.

[0070]

The epoxy group-containing compounds described above can be used alone or in combination of two or more kinds thereof. A content of the epoxy group of the epoxy group-containing compound described above shall not specifically be restricted, and the epoxy equivalent falls suitably in a range of usually 100 to 3,000, preferably 100 to 1,500.

[0071]

The alkoxysilyl group-containing compound which can be used as the compound [B] is a compound having two or more alkoxysilyl groups in a molecule and includes, for example, alkoxysilanes having no polymerizable unsaturated groups such as dimethoxydimethylsilane, dimethoxydiethylsilane, dimethoxydiphenylsilane, diethoxydimethylsilane, trimethoxymethylsilane, trimethoxyethylsilane, trimethoxypropylsilane, trimethoxyphenylsilane, tetramethoxysilane, tetraethoxysilane, tetrabutoxysilane and dimethoxydiethoxysilane; polymerizable unsaturated group-containing alkoxysilanes such as vinyltrimethoxysilane, vinyltriethoxysilane, vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, γ-(meth)acryloyloxypropyltrimethoxysilane, γ-(meth)acryloyloxypropylmethyldimethoxysilane, γ-(meth)acryloyloxypropylmethyldiethoxysilane, γ-(meth)acryloyloxypropyltriethoxysilane, β-(meth)acryloyloxyethyltrimethoxysilane and γ-(meth)acryloyloxybutylphenyldimethoxysilane; partially condensed products of the above alkoxysilanes having no polymerizable unsaturated groups and/or the polymerizable unsaturated group-containing alkoxysilanes described above; and copolymers of the polymerizable unsaturated group-containing alkoxysilanes described above with polymerizable unsaturated monomers which can be copolymerized with the above alkoxysilanes.

[0072]

The polymerizable unsaturated monomers capable of being copolymerized with the alkoxysilanes which are the monomer components for the copolymers described above include monomers other than the alkoxysilyl group-containing polymerizable unsaturated compounds capable of being used as the "other polymerizable unsaturated monomers" which are copolymerized with the epoxy group-containing polymerizable unsaturated monomers when the epoxy group-containing compounds described above are copolymers.

[0073]

Capable of being given as the compound (hereinafter, abbreviated as a "polyacid anhydride") having two or more carboxylic anhydride groups which can be used as the compound [B] are, for example, pyromellitic

anhydride, a condensation product (ethylenebis[anhydrotrimellitate]) of one mole of ethylene glycol and 2 moles of trimellitic anhydride, and a condensation product (glycerintris[anhydrotrimellitate]) of one mole of glycerin and 3 moles of trimellitic anhydride; linear or cyclic polyacid anhydrides obtained by subjecting polybasic acids such as succinic acid, adipic acid, azelaic acid, sebacic acid, dodecanedioic acid, dimer acid, ethyl-octadecanedioic acid, phenyl-hexadecanedioic acid and 1,4-cyclohexanedicarboxylic acid to intermolecular condensation; and polymers comprising a polymerizable unsaturated acid anhydride such as maleic anhydride and tetrahydrophthalic anhydride as a single monomer component. The monomers other than the polymerizable unsaturated acid anhydrides which can form the above polymers include, for example, alkyl (meth)acrylates having 1 to 24 carbon atoms such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl acrylate, n-octyl (meth)acrylate, lauryl (meth)acrylate, tridecyl (meth)acrylate and stearyl (meth)acrylate; acrylic acid, methacrylic acid, crotonic acid, acrylonitrile, methacrylonitrile, tricyclodecanyl (meth)acrylate, isobornyl (meth)acrylate, vinyl acetate, Beova Monomer (manufactured by Shell Chemical Co., Ltd.), styrene, vinyltoluene and α-methylstyrene.

[0074]

A content of the acid anhydride groups in the polyacid anhydrides described above shall not specifically be restricted, and the whole acid value based on the acid anhydride groups falls suitably in a range of usually 50 to 1,100 mg KOH/g, preferably 80 to 800 mg KOH/g.

[0075]

The compounds [B] described above can be used alone or in combination of two or more kinds thereof.

Curable composition

The curable composition of the present invention comprises the polyorthoester [A] and the compound [B] each described above as the essential components. A blending proportion of the above components [A] and [B] shall not specifically be restricted and falls suitably in a range of usually 95/5 to 20/80,

preferably 90/10 to 30/70 in terms of a solid matter weight ratio of [A] / [B].

[0076]

In addition to the components [A] and [B] described above, the curable composition of the present invention can suitably contain, if necessary, an acid catalyst, an organic solvent, a curing catalyst, a pigment, a UV absorber, a coated surface-controlling agent, an antioxidant, a fluidity-controlling agent and a wax.

[0077]

The acid catalyst described above is a catalyst for accelerating a reaction of deblocking an orthoester group to reproduce a hydroxyl group. The kind thereof shall not specifically be restricted, and capable of being given are, for example, inorganic acids such as hydrochloric acid, sulfuric acid and nitric acid; sulfonic acid compounds such as methanesulfonic acid, ethanesulfonic acid, paratoluenesulfonic acid, dodecylbenzenesulfonic acid, dinonylnaphthalenesulfonic acid and dinonylnaphthalenedisulfonic acid; compounds obtained by neutralizing the sulfonic acid compounds described above with bases such as amines; esters of the sulfonic acid compounds described above with primary, secondary or tertiary alcohols such as n-propanol, n-butanol, n-hexanol, n-octanol, isopropanol, 2-butanol, 2-hexanol, 2-octanol, cyclohexanol and tert-butanol; β-hydroxyalkylsulfonic acid esters obtained by reacting the sulfonic acid compounds described above with oxirane group-containing compounds such as glycidyl acetate and butyl glycidyl ether; carboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid, 2-ethylhexanoic acid and octanoic acid; organic phosphoric acid base compounds such as monobutyl phosphate, dibutyl phosphate, monoisopropyl phosphate, diisopropyl phosphate, monooctyl phosphate, dioctyl phosphate, monodecyl phosphate, didecyl phosphate, metaphosphoric acid, orthophosphoric acid, pyrophosphoric acid, trimethyl phosphate, triethyl phosphate, tributyl phosphate, trioctyl phosphate, tributoxyethyl phosphate, tris·chloroethyl phosphate, triphenyl phosphate and tricresyl phosphate; light latent acid-generating agents which generate acids by irradiating with UV rays such as Cyracure UVI-6970, ditto UVI-6974 and ditto UVI-6990 (all described above are manufactured by Union Carbide Co., Ltd., U.S.A.), Irgacure 261 and

ditto 264 (all described above are manufactured by Ciba Specialty Chemicals Co., Ltd.), CIT-1682 (manufactured by Nippon Soda Co., Ltd.), BBI-102 (manufactured by Midori Kagaku Co., Ltd.) and Adeka Optomer SP-150 and ditto SP-170 (all described above are manufactured by Asahi Denka Kogyo K.K.); and Lewis acids.

[0078]

The composition of the present invention can usually be a composition of a non-solvent or organic solvent type. When it is the composition of an organic solvent type, solvents which can dissolve or disperse the respective components of the composition of the present invention can be used as the organic solvents, and capable of being given are, for example, hydrocarbon base solvents such as heptane, toluene, xylene, octane and mineral spirits; ester base solvents such as ethyl acetate, n-butyl acetate, isobutyl acetate, ethylene glycol monomethyl ether acetate and diethylene glycol monobutyl ether acetate; ketone base solvents such as methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone and cyclohexanone; alcohol base solvents such as methanol, ethanol, isopropanol, n-butanol, sec-butanol and isobutanol; ether base solvents such as n-butyl ether, dioxane, ethylene glycol monomethyl ether and ethylene glycol monoethyl ether; and aromatic petroleum base solvents such as Swasol 310, Swasol 1000 and Swasol 1500 (all described above are manufactured by Cosmo Oil Co., Ltd.) and Shellsol A (manufactured by Shell Chemical Co., Ltd.). These organic solvents can be used alone or in combination of two or more kinds thereof.

[0079]

The curing catalyst described above which is blended, if necessary, with the composition of the present invention is intended for accelerating the curing reaction of the composition, and suited when the compound [B] is a blocked polyisocyanate compound is, for example, a curing catalyst which promotes the dissociation of a blocking agent in the blocked polyisocyanate compound which is a curing agent. Capable of being given as the suited curing catalyst are, for example, organic metal catalysts such as tin octanoate, dibutyltin di(2-ethylhexanoate), dioctyltin di(2-ethylhexanoate), dioctyltin diacetate, dibutyltin dilaurate, dibutyltin oxide, dioctyltin oxide and lead

2-ethylhexanoate.

[0080]

When the compound [B] is an amino resin such as a melamine resin, particularly a methyl-etherified or methyl ether and butyl ether-mixed etherified melamine resin having a low molecular weight, phosphoric acid, a sulfonic acid compound or an amine-neutralized product of the sulfonic acid compound is suitably used as the curing catalyst. The representative examples of the sulfonic acid compound include p-toluenesulfonic acid, dodecylbenzenesulfonic acid, dinonylnaphthalenesulfonic acid and dinonylnaphthalenedisulfonic acid. The amine in the amine-neutralized product of the sulfonic acid compound may be any one of primary amines, secondary amines and tertiary amines.

[0081]

The curing catalyst used when the compound [B] is the epoxy group-containing compound includes, for example, chelating compounds such as tetrakis(acetylacetonato)zirconium, cobalt acetylacetonate, tris(acetylacetonato)aluminum and manganese acetylacetonate; chelating reaction products of compounds having a β–hydroxyamino structure with lead (II) oxide; metal carboxylates such as lead 2-ethylhexanoate, lead secanoate, lead naphthenoate, lead octanoate, lead acetate, lead lactate and zirconium octanoate; and imidazole compounds such as imidazole, 2-methylimidazole, 2-isopropylimidazole, 2-undecylimidazole and 2-phenylimidazole.

[0082]

The curing catalyst used when the compound [B] is the alkoxysilyl group-containing compound includes, for example, organic sulfonic acid compounds such as dodecylbenzenesulfonic acid, paratoluenesulfonic acid, dinonylnaphthalenesulfonic acid and trifluorosulfonic acid; amine-neutralized products of these organic sulfonic acid compounds; and phosphoric acid base compounds such as monobutyl phosphate, dibutyl phosphate, monoisopropyl phosphate, diisopropyl phosphate, monooctyl phosphate, dioctyl phosphate, monodecyl phosphate, didecyl phosphate, metaphosphoric acid, orthophosphoric acid, pyrophosphoric acid, trimethyl phosphate, triethyl phosphate, tributyl phosphate, trioctyl phosphate, tributoxyethyl phosphate, tris-chloroethyl phosphate, triphenyl phosphate and tricresyl phosphate.

[0083]

The curing catalyst used when the compound [B] is the polyacid anhydride includes, for example, quaternary salt catalysts such as tetraethylammonium bromide, tetrabutylammonium bromide, tetraethylammonium chloride, tetrabutylammonium fluoride, tetrabutylphosphonium bromide and triphenylbenzylphosphonium chloride; and amines such as triethylamine and tributylamine.

[0084]

Capable of being given as the pigment compounded, if necessary, with the composition of the present invention are inorganic color pigments such as titanium white, carbon black, red iron oxide and titanium yellow; organic color pigments such as quinacridone red, azo red, phthalocyanine blue, phthalocyanine green and organic yellow pigments; brilliant pigments such as aluminum powder and brilliant mica powder; extender pigments such as silica powder, calcium carbonate, barium sulfate, mica, clay and talc; and rust preventive pigments such as calcium ion-exchanged silica, phosphate base rust preventive pigments and chromate base pigments.

[0085]

The composition of the present invention can suitably be used for uses in coating material compositions, adhesives and inks, particularly as a coating material composition. The curing conditions of the composition of the present invention shall not specifically be restricted. Usually, when the curing time is 5 minutes or longer, the curing temperature falls suitably in a range of a room temperature (about 0°C) to about 200°C, particularly about 60°C to about 180°C, and when the curing time is shorter than 5 minutes, the curing temperature falls suitably in a range of about 60°C to about 300°C, particularly about 80°C to about 260°C.

[0086]

[Examples]

The present invention shall more specifically be explained below with reference to examples and comparative examples, and "parts" and "%" mean "parts by weight" and "% by weight" respectively.

[0087]

Synthesis Example 1: Production of polyester solution

A reactor equipped with a stirrer, a condenser, a temperature-controlling device, a water separator, a fractionating column, a nitrogen-introducing tube and a solvent-recovering device was charged with 161 parts of 1,6-hexanediol, 351 parts of 1,4-dimethylolcyclohexane, 146 parts of trimethylolpropane, 114 parts of adipic acid, 300 parts of hexahydrophthalic anhydride and 243 parts of isophthalic acid, and the reactor was substituted with nitrogen and then started to be heated. The temperature was elevated at a fixed rate from 170°C to 230°C in 3 hours while removing condensation water and then maintained at 230°C for one hour. Thereafter, 50 parts of xylene was added, and the reaction was further promoted for 3 hours while maintaining at 230°C and removing condensation water by means of the water separator. Then, the reactor was cooled down, and 464 parts of xylene was added thereto to obtain a polyester solution (PE-1) having a non-volatile matter content of about 69% and a Gardner viscosity (20°C) of X. The resulting resin (solid matter) had a resin acid value of 6.5 mg KOH/g, a hydroxyl group value of 120 mg KOH/g, a number average molecular weight of 1,800 and a weight average molecular weight of 5,200.

[0088]

Synthesis Example 2: Production of acrylic resin solution

A reactor equipped with a stirrer, a condenser, a temperature-controlling device, a nitrogen-introducing tube and a dropping funnel was charged with 983 parts of xylene and 240 parts of 3-methoxybutyl acetate, and the reactor was substituted with nitrogen, heated and maintained at 135°C. Added drop by drop thereto in 4 hours was a mixture comprising 600 parts of styrene, 636 parts of isobutyl methacrylate, 552 parts of 2-ethylhexyl acrylate, 612 parts of 2-hydroxyethyl methacrylate and 192 parts of azobisisobutyronitrile. After finishing dropping, the solution was ripened at 135°C for 30 minutes, and then, a mixed solution comprising 168 parts of xylene and 12 parts of azobisisobutyronitrile was added drop by drop thereto in one hour. Then, the solution was maintained at 135°C for 30 minutes to obtain an acrylic resin solution (AR-1) having a non-volatile matter content of about 63% and a Gardner viscosity (20°C) of U^+. The resulting resin (solid matter)

had a hydroxyl group value of 110 mg KOH/g, a number average molecular weight of 1,900 and a weight average molecular weight of 4,300.

[0089]

Production Example 1

A reactor equipped with a stirrer, a condenser, a temperature-controlling device and a solvent-recovering device was charged with 424 parts of methyl orthoformate, 640 parts of 2-butyl-2-ethyl-1,3-propanediol, 136 parts of pentaerythritol and 4 parts of a 90% formic acid aqueous solution and maintained at about 85°C for one hour while distilling off methanol produced by alcohol exchange reaction. Then, the temperature was elevated up to 190°C in 2 hours, and 365 parts of methanol was recovered to obtain a colorless and liquid polyorthoester. The polyorthoester thus obtained had a Gardner viscosity of X^+ and a weight average molecular weight of 1,540.

[0090]

Production Examples 2 to 12 and Comparative Production Examples 1 to 3

The reaction was carried out in the same manner as in Production Example 1 to obtain the respective polyorthoesters, except that in Production Example 1, the blended raw material compositions were changed as shown in the following Table 1. In Production Examples 6 and 7, distilled off was a part of an organic solvent (xylene) contained in the raw material in addition to alcohol produced by alcohol exchange. The polyorthoester solution obtained in Production Example 6 had a solid content of about 74%, and the polyorthoester solution obtained in Production Example 7 had a solid content of about 68%.

[0091]

The polyorthoester obtained in Comparative Production Example 1 had a solid content of about 100% and crystallized. In Comparative Production Example 2 and Comparative Production Example 3, gelation took place in the middle of the reaction.

[0092]

All the polyorthoesters obtained in Production Examples 1 to 5 and 8 to 12 were colorless and liquid polyorthoesters and had a solid content of

substantially about 100%. In Production Example 6 and Comparative Production Example 2, the acid catalyst was not blended, but a carboxyl group contained in the resin in the polyester solution (PE-1) works as a catalyst.

[0093]

A remark in Table 1 means the following:

(Remark 1) Placcel 305: polycaprolactonepolyol, manufactured by Daicel Chemical Industries, Ltd.

[0094]
[Table 1]

Table 1

		Example												Comparative Example		
		1	2	3	4	5	6	7	8	9	10	11	12	1	2	3
Component (A)	Methyl orthoformate	424					106			424	636	424	424	212	35	
	Methyl orthoacetate			480	480	480		120	360							40
	Ethyl orthoformate		592													
Component (B)	2-Butyl-2-ethyl-1,3-propanediol	640	640	640			160	160		320	160	640				
	Neopentyl glycol				416				312							
	2,2,4-trimethyl-1,3-pentanediol					584										
	1,2-Hexanediol												472			

To be continued

Table 1 (continued)

		Example												Comparative Example		
		1	2	3	4	5	6	7	8	9	10	11	12	1	2	3
Component (C)	Pentaerythritol	136	136	136	136	136				68	136	136	136	136		
	Polyester solution (PE-1)						668								668	
	Acrylic resin solution (AR-1)							850								850
	Placcel 305 (remark 1)								550							
	Trimethylol-propane									268	536					
Acid catalyst	90 % formic acid aqueous solution	4	4	4	4	4		2	3	8	6		4	4		2
	p-Toluenesulfonic acid											1				
Recovered alcohol	Methanol	365		360	366	342	91	92	267	362	523	341	360	130	16	22
	Ethanol		539													
Properties of polyorthoester (solution)	Gardner viscosity	X^+	W	M	G^+	$A1^+$	Z	UV	S	OP	W	Y	T	Crystal -lized	Gelled	Gelled
	Weight average molecular weight	1540	1420	1060	430	410	6950	5620	1640	1250	1600	1590	1270	—	—	—

[0095]

A weight average molecular weight, a hydroxyl group value and a viscosity of the polyorthoesters obtained in Production Examples 1 and 11 were compared with those of Placcel 303, and the results thereof are shown in the following Table 2.

[0096]

A remark in Table 2 means the following:

(Remark 2) Placcel 303: polycaprolactonepolyol, manufactured by Daicel Chemical Industries, Ltd.

[0097]

[Table 2]

Table 2

	Weight average molecular weight (after hydrolysis)	Hydroxyl group value* (mg KOH/g)	Viscosity (mPa·s)
Polyorthoester of Production Example 1	1540	550	1350
Polyorthoester of Production Example 11	1590	550	1420
Praccel 303 (remark 2)	610	540	1800

* The hydroxyl group value represents a hydroxyl group value obtained after hydrolysis (a hydroxyl group value after recovering a hydroxyl group) in polyorthoesters.

[0098]

It is apparent from the results shown in Table 1 that all the polyorthoesters obtained in Production Examples 2 to 5 and Production Examples 8 to 10 and 12 had a lower Gardner viscosity than that of the polyorthoester obtained in Production Example 1.

[0099]

The polyorthoester obtained in Production Example 6 had a solid content of about 74%, and when the solid content was controlled to 69% by adding xylene to the above polyorthoester, the Gardner viscosity was V, which

was lower than the viscosity X of the polyester solution (PE-1) having a solid content of 69% used in Production Example 6.

[0100]

Further, the polyorthoester solution obtained in Production Example 7 had a solid content of about 68%, and when the solid content was controlled to 63% by adding xylene to the above polyorthoester, the Gardner viscosity was O, which was lower than the viscosity U^+ of the acrylic resin solution (AR-1) having a solid content of 63% used as a raw material in Production Example 7.

[0101]

Production of compound having two or more groups having reactivity with a hydroxyl group in a molecule

Production Example 13

A reactor equipped with a stirrer, a condenser, a temperature-controlling device, a nitrogen-introducing tube and a dropping funnel was charged with 983 parts of xylene and 240 parts of 3-methoxybutyl acetate, and the reactor was substituted with nitrogen, heated and maintained at 135°C. Added drop by drop thereto in 4 hours was a mixture comprising 720 parts of styrene, 720 parts of 2-ethylhexyl acrylate, 960 parts of glycidyl methacrylate and 192 parts of azobisisobutyronitrile. After finishing dropping, the solution was ripened at 135°C for 30 minutes, and then, a mixed solution comprising 168 parts of xylene and 12 parts of azobisisobutyronitrile was added drop by drop in one hour. Then, the solution was maintained at 135°C for 30 minutes to obtain an epoxy group-containing acrylic resin solution (B-1) having a non-volatile matter content of about 63% and a Gardner viscosity (20°C) of S. The resulting resin (solid matter) had an epoxy equivalent of about 370, a number average molecular weight of 2,100 and a weight average molecular weight of 4,900.

[0102]

Production Example 14

A reactor equipped with a stirrer, a condenser, a temperature-controlling device, a nitrogen-introducing tube and a dropping funnel was charged with 983 parts of xylene and 240 parts of 3-methoxybutyl acetate, and the reactor was substituted with nitrogen, heated and maintained

at 135°C. Added drop by drop thereto in 4 hours was a mixture comprising 600 parts of styrene, 600 parts of maleic anhydride, 1,200 parts of n-butyl acrylate and 192 parts of azobisisobutyronitrile. After finishing dropping, the solution was ripened at 135°C for 30 minutes, and then, a mixed solution comprising 168 parts of xylene and 12 parts of azobisisobutyronitrile was added drop by drop in one hour. Then, the solution was maintained at 135°C for 30 minutes to obtain an acid anhydride group-containing acrylic resin solution (B-2) having a non-volatile matter content of about 63% and a Gardner viscosity (20°C) of R⁻. The resulting resin (solid matter) had a whole acid value of about 266 mg KOH/g, a half acid value of about 138 mg KOH/g, a number average molecular weight of 1,900 and a weight average molecular weight of 4,800.

[0103]

Production Example 15

A reactor equipped with a stirrer, a condenser, a temperature-controlling device, a nitrogen-introducing tube and a dropping funnel was charged with 983 parts of xylene and 240 parts of 3-methoxybutyl acetate, and the reactor was substituted with nitrogen, heated and maintained at 135°C. Added drop by drop thereto in 4 hours was a mixture comprising 720 parts of styrene, 720 parts of n-butyl methacrylate, 480 parts of 2-ethylhexyl acrylate, 480 parts of γ-methacryloyloxypropyltrimethoxysilane and 192 parts of azobisisobutyronitrile. After finishing dropping, the solution was ripened at 135°C for 30 minutes, and then, a mixed solution comprising 168 parts of xylene and 12 parts of azobisisobutyronitrile was added drop by drop in one hour. Then, the solution was maintained at 135°C for 30 minutes to obtain an alkoxysilyl group-containing acrylic resin solution (B-3) having a non-volatile matter content of about 63% and a Gardner viscosity (20°C) of W. The resulting resin (solid matter) had a number average molecular weight of 2,800 and a weight average molecular weight of 5,500.

[0104]

Production Example 16

A reactor equipped with a stirrer, a condenser, a temperature-controlling device, a nitrogen-introducing tube and a dropping funnel was charged with 983 parts of xylene and 240 parts of 3-methoxybutyl

acetate, and the reactor was substituted with nitrogen, heated and maintained at 135°C. Added drop by drop thereto in 4 hours was a mixture comprising 480 parts of styrene, 480 parts of maleic anhydride, 480 parts of glycidyl methacrylate, 960 parts of 2-ethylhexyl acrylate and 192 parts of azobisisobutyronitrile. After finishing dropping, the solution was ripened at 135°C for 30 minutes, and then, a mixed solution comprising 168 parts of xylene and 12 parts of azobisisobutyronitrile was added drop by drop in one hour. Then, the solution was maintained at 135°C for 30 minutes to obtain an acrylic resin solution (B-4) containing an epoxy group and acid anhydride group and having a non-volatile matter content of about 63% and a Gardner viscosity (20°C) of S^+. The resulting resin (solid matter) had an epoxy equivalent of about 710, a half acid value of about 102 mg KOH/g, a number average molecular weight of 2,200 and a weight average molecular weight of 4,900.

[0105]

Preparation of curable composition

Example 1

The polyorthoester 100 parts obtained in Production Example 1 was blended with 191 parts of Desmodur N-3300 (triisocyanurate of hexamethylenediisocyanate, manufactured by Sumitomo Bayer Urethane Co., Ltd.) and 11.6 parts of Nacure 5543 (sulfonate base acid catalyst solution, active ingredient: about 25%, manufactured by King Industries Inc., U.S.A.), and the solution was homogeneously mixed to obtain a curable composition.

[0106]

Examples 2 to 22 and Comparative Examples 1 and 2

The same operation as in Example 1 was carried out to obtain the respective curable compositions, except that in Example 1, the blending composition was changed as shown in the following Table 3.

[0107]

The remarks in Table 3 mean the following respectively:

[0108]

(Remark 1) and (Remark 2) mean the same as those described above.

[0109]

(Remark 3) Cymel 303: methyl-etherified melamine resin, solid content: about 100%, manufactured by Mitsui Cytec Co., Ltd.

[0110]

(Remark 4) Cymel 325: methyl-etherified melamine resin, solid content: about 80%, manufactured by Mitsui Cytec Co., Ltd.

[0111]

(Remark 5) SB-20AH: polyacid anhydride of ethyl-octadecanedioic acid, condensation degree: about 4.1, manufactured by Okamura Oil Mill, Ltd.

[0112]

The respective curable compositions obtained in Examples 1 to 22 and Comparative Examples 1 and 2 were tested for a compatibility and a solvent resistance and a gel ratio of the cured coating films based on the following test methods. Further, the respective curable compositions obtained in Examples 1 to 12 and Comparative Examples 1 and 2 were tested as well for a pot life. The test results thereof are shown in the following Table 3. Furthermore, the Gardener viscosities of the respective curable compositions obtained in Examples 1 to 12 and Comparative Examples 1 and 2 are shown as well in Table 3.

[0113]

Test methods

Compatibility:

Each curable composition was put in a test tube to visually observe the appearance thereof, and it was evaluated according to the following criteria:

[0114]

O : not cloudy and transparent, and compatibility is good

Δ : cloudy, and compatibility is inferior

× : phases are separated, and compatibility is notably inferior

[0115]

Solvent resistance:

The curable composition was coated on a polished cold rolled steel plate so that a dried film thickness was about 30 μm and dried at 140°C for 30 minutes (only the composition prepared in Example 18 was dried at 160°C for

30 minutes) to obtain a coating film. The surface of the coated film was rubbed in a length of about 5 cm at a load of about 1 kg/cm^2 by 20 reciprocations with a three-folded gauze impregnated with xylene, and then the state of the surface of the coated film was observed and evaluated according to the following criteria:

[0116]

O : coating film has no scratches and dull glossiness and is of a good state

Δ : coating film has slightly scratches or slightly dull glossiness and is of a little inferior state

× : coating film is dissolved or markedly scratched

[0117]

Gel ratio:

The curable composition was coated on a teflon sheet so that a dried film thickness was about 30μm and dried at 140°C for 30 minutes (only the composition prepared in Example 18 was dried at 160°C for 30 minutes), and the coating film was peeled off to obtain a free coating film. The free coating film was extracted under refluxing in acetone for 6 hours, and the gel ratio (%) was determined from the coating film weights before and after extraction according to the following equation:

[0118]

$$\text{gel ratio (\%)} = \frac{\text{(coating film weight after extraction)}}{\text{(coating film weight before extraction)}} \times 100$$

Pot life:

The curable composition was put in a glass bottle of 100 ml, and the bottle was sealed up and left standing in a dark place of 30°C to measure the viscosity every 6 hours to determine time passing until the viscosity grew larger to lose fluidity:

[0119]

O : fluidity is kept even after passage of 24 hours

● : fluidity is kept after 6 hours, but fluidity is lost after 24 hours

× : fluidity is lost within 6 hours

[0120]
[Table 3]

Table 3

		Example												Comparative Example	
		1	2	3	4	5	6	7	8	9	10	11	12	1	2
Polyortho-ester	Kind (Production Example No.)	1	2	3	4	5	6	7	8	9	10	11	12		
	Amount	100	100	100	100	100	131	143	100	100	100	100	100		
Praccel 305 (remark 1)															100
Praccel 303 (remark 2)														100	
Desmodur N3300		191		181	240	191	62	57	127	227	265	191		187	106
Lysinetriisocyanate			90										105		
Cymel 303 (remark 3)															
Cymel 325 (remark 4)															
SB-20AH (remark 5)															

To be continued

Table 3 (continued)

		Example												Comparative Example	
		1	2	3	4	5	6	7	8	9	10	11	12	1	2
Acrylic resin solution having a non-volatile matter content of 63%	(B-1)														
	(B-2)														
	(B-3)														
	(B-4)														
Nacure 5543		11.6	7.6	11.2	13.6	11.6	6.5	6.3	9.1	13.1	14.6	11.6	8.2	11.5	8.2
Lead 2-ethylhexanoate															
Tetrabutylammonium bromide															
Test results	Gardner viscosity (25°C)	V	F	Q	KL	G^-	Y	T^+	S	QR	UV	V^+	C^-	Z	W
	Compatibility	O	O	O	O	O	O	O	O	O	O	O	O	×	Δ
	Solvent resistance	O	O	O	O	O	O	O	O	O	O	O	O	×	Δ
	Gel ratio (%)	97	99	96	98	95	95	97	99	99	98	99	98	85	96
	Pot life	O	O	O	O	O	O	O	O	O	O	O	O	×	×

To be continued

[0121]
[Table 4]

Table 3 (continued)

		Example									
		13	14	15	16	17	18	19	20	21	22
Polyortho-ester	Kind (Production Example No.)	1	3	8	4	1	1	1	7	1	1
	Amount	100	100	100	100	100	20	20	143	20	20
Placcel 305 (remark 1)											
Placcel 303 (remark 2)											
Desmodur N3300						191					
Lysinetriisocyanate											
Cymel 303 (remark 3)		67	67	67		20					
Cymel 325 (remark 4)					84						
SB-20AH (remark 5)									20		

To be continued

Table 3 (continued)

		Example									
		13	14	15	16	17	18	19	20	21	22
Acrylic resin solution having a non-volatile matter content of 63%	(B-1)						123				
	(B-2)							123			
	(B-3)									123	
	(B-4)										123
Nacure 5543		6.7	6.7	6.7	6.7	12.4	4	4	4.8	4	4
Lead 2-ethylhexanoate							3				
Tetrabutylammonium bromide								1.5	1.5		1.5
Test results	Compatibility	O	O	O	O	O	O	O	O	O	O
	Solvent resistance	O	O	O	O	O	O	O	O	O	O
	Gel ratio (%)	99	99	99	99	99	94	95	97	98	99

[0122]

[Effect of the invention]

The curable composition of the present invention is a composition comprising a polyorthoester and a curing agent. The polyorthoester comprises an orthoester structure introduced into a hydroxyl group part of a hydroxyl group-containing compound and has a high degree of freedom in molecular design, and it can be applied to various fields and is industrially very useful. The curable composition of the present invention comprises a structure in which a hydroxyl group in a hydroxyl group-containing compound is blocked by the orthoester and therefore is free of problems originating in a hydroxyl group, for example, a problem on a rise in viscosity of the curable composition, so that it is excellent in compatibility, wetting property to a base material and storage stability.

[Document Name] Abstract

[Abstract]

[Subject]

The present invention is to provide a curable composition using a polyorthoester which has a high degree of freedom in molecular design and a low viscosity and is readily controlled in molecular weight, and a curable composition which is free of problems originating in a hydroxyl group, for example, a problem on a rise in viscosity of the curable composition and is excellent in compatibility, wetting property to a base material and storage stability.

[Means for Solution]

A curable composition comprising [A] a polyorthoester which is prepared by reacting (a) an orthoester such as methyl orthoformate, ethyl orthoformate, methyl orthoacetate or ethyl orthoacetate, (b) at least one glycol compound selected from α-glycols and β-glycols, and (c) a hydroxyl group-containing compound having at least two hydroxyl groups in a molecule other than the above (b); and [B] a curing agent having a relativity with a hydroxyl group.

[Selected Drawing]

None